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MONODEUTERATED METHANE IN THE OUTER SOLAR SYSTEM

II. ITS DETECTION ON URANUS AT 1.6 μ m.

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ABSTRACT

We have detected the $3\nu_2$ band of CH_3D in the spectrum of Uranus recorded with the Fourier Transform Spectrometer (FTS) at the 4-meter Mayall telescope of Kitt Peak National Observatory (KPNO). Using a scattering-model atmosphere and spectral synthesis techniques, we derived a bulk $\text{CH}_3\text{D}/\text{CH}_4$ mixing ratio of $3.6^{+3.6}_{-1.8} \times 10^{-4}$ from these observations that suggests a deuterium enhancement in methane relative to that observed on Jupiter.

I. INTRODUCTION

Deuterium in the atmosphere of Uranus has been studied only via measurements of the exceedingly weak dipole lines of hydrogen-deuteride (HD) seen in the visible region of the spectrum (Macy and Smith 1978; Trafton and Ramsay 1980; Cochran and Smith 1983). The other sensitive indicator of deuterium in the outer solar system is monodeuterated methane (CH_3D), but the two bands normally used to study this molecule, ν_2 near 2200 cm^{-1} and ν_6 near 1161 cm^{-1} , have not been detected in Uranus.

In a previous publication (Lutz et al. 1981), we reported the discovery of a new system of CH_3D centered near 6425 cm^{-1} and proposed it as a promising alternative to ν_2 and ν_6 in outer planet atmosphere searches, particularly since in this spectral region the common

problem of blending with the ubiquitous lines of methane appeared tractable. Subsequently in a laboratory investigation described in Paper I of this series (Lutz, de Bergh, and Maillard 1983), we carried out a detailed rotational analysis and showed that the main features form a simple parallel band that is best characterized as the second overtone of ν_2 , thus confirming its viability as an atmospheric tracer of CH_3D . In this paper we describe our search for this new band, $3\nu_2$, in the spectrum of Uranus and estimate the abundance of CH_3D in its atmosphere.

II. PLANETARY OBSERVATIONS

Two sets of new spectroscopic observations of Uranus were used in our search for CH_3D . Both were recorded with the FTS at the coude focus of the 4-meter Mayall telescope at KPNO, and all the interferograms were transformed using the standard KPNO routines at the Tucson facility. The details of the instrument, its operating characteristics, and the reduction procedure can be found in the KPNO-FTS users' handbook. Both sets of observations used nearly identical instrumental configurations, differing primarily in resolution. The essential common features included the use of the CaF_2 beam splitter with liquid-helium-cooled InSb detectors "C" and "D" in the normal dual beam, sky-switched combination using circular

apertures 3"75 in diameter. A narrow-band blocking filter peaked at 1.6 μm was used to limit the spectral acceptance of the detectors and to maximize the signal-to-noise ratio of the spectra. Between this filter and the strong methane absorptions defining the planetary window, the effective spectral coverage was limited to the range 6100 to 6700 cm^{-1} .

The first set of observations was obtained on the nights of U.T. 1981 March 13-15 with an unapodized full-width-at-half-maximum (FWHM) resolution of 2.1 cm^{-1} . The spectra were recorded in time blocks of approximately one hour to be selectively co-added after transformation. The total integration time was 1.7 hours, effecting a total signal-to-noise (S/σ) of ~60 in the final co-added spectrum. This final spectrum provided the first unequivocal detection of CH_3D on Uranus and indicated a need for still higher resolution to derive a meaningful $\text{CH}_3\text{D}/\text{CH}_4$ mixing ratio.

The second set of spectra were obtained during the week of U.T. 1982 June 2-7, with an unapodized FWHM resolution of 1.2 cm^{-1} , again in one-hour blocks. In this case the total effective integration time for the co-added spectra was 3.8 hours, yielding a total signal-to-noise of near 80. This final 1.2 cm^{-1} spectrum is the basis of the analysis described in this paper.

To determine the effects of low temperature on the methane absorption in the 6425 cm^{-1} region, we also recorded high-resolution

(0.1 cm^{-1} FWHM) spectra of Saturn during the 1981 run for comparison with our room-temperature laboratory data described in section III. In this case, the object aperture ($3''75$ in diameter) was placed on the central meridian as close to the equator as possible without accepting a contribution from the rings. A total integration time of seven hours yielded a signal-to-noise of about 150 in the co-added spectrum. In addition, lunar spectra were recorded at each resolution during their respective runs to account for terrestrial and solar contamination in the planetary spectra, and in 1982 a series of diffused solar spectra were obtained for a similar comparison.

III. LABORATORY OBSERVATIONS

For an accurate quantitative analysis of trace constituents in a planetary atmosphere, it is essential to account for all the faint absorptions observed in its observed spectrum. In the outer planets, the region of the $3\nu_2$ band of CH_3D near 6425 cm^{-1} is dominated by very weak, rotationally unassigned features of methane that can be studied in the laboratory only at very long pathlengths and very high signal-to-noise. These methane features were the subject of a laboratory investigation carried out in association with this project and described in this section.

Several room-temperature spectra of CH_4 were recorded with the FTS at the McMath telescope at the National Solar Observatory in Tucson. The 6-meter-long "JPL" absorption cell was employed at a pathlength of 434 meters for several pressures between 15 and 500 torr, and an additional spectrum was obtained with a pathlength of 217 meters and a pressure of 15 torr. The signal-to-noise of each spectrum is 1000 or more, and the maximum spectral resolution obtained was 9 mcm^{-1} .

Intensities for 610 lines of methane (including those of CH_3D present in normal isotopic abundance) detected in the spectral range $6413\text{--}6484 \text{ cm}^{-1}$ were derived by fitting the line profiles in the 15 torr spectra with a Voigt function, assuming a mean self-broadening coefficient of $0.085 \text{ cm}^{-1} \text{ atm}$ at 295 K (Varanasi 1971). Significant line blending for many of the features prevented us from doing a more refined analysis, but the accuracy of this approach was checked by computing spectra for 100 and 200 torr based on our 15 torr results and comparing them with the relevant laboratory spectra recorded. Figure 1 presents a comparison of the synthetic (dashed line) and observed (solid line) spectra for 200 torr and illustrates the level of agreement that was obtained.

Using the line positions and rotational assignments given in Paper I for the $3\nu_2$ region of CH_3D and the line intensities and pressure-broadening coefficients measured by Lutz (1985) and adopting

a telluric $\text{CH}_3\text{D}/\text{CH}_4$ ratio of 5.5×10^{-4} derived from mass spectroscopic measurements of ordinary methane (Lutz et al. 1981), we were able to determine which features detected in our methane spectra are actually pure lines of CH_3D or CH_4 and which others are blends due to both. In Figure 2 we show a small region ($6424\text{--}6431\text{ cm}^{-1}$) of the methane spectrum recorded with 434 m pathlength at 200 torr to illustrate this technique. The shaded features represent the contribution of Q-branch lines of the $3\nu_2$ band of CH_3D , denoted by their rotational adjustments to J_K , to the observed spectra.

Knowledge of the low temperature dependences of these weak CH_4 features is needed for interpretation of the Uranian absorptions, but such behavior is not predictable without their quantum assignments. Furthermore, cold laboratory spectra at column densities comparable to those recorded at room temperature are lacking for an empirical description. However, Saturn can serve as an adequate substitute source for these essential data.

The large amounts of CH_4 present in the Saturn atmosphere make the intrinsically weak CH_4 absorptions (intensity between 2×10^{-6} and $4 \times 10^{-4}\text{ cm}^{-1}/\text{m}\cdot\text{am}$) very apparent in its spectrum (Figure 3), and the temperatures of those regions of its atmosphere probed by near-infrared spectra are probably close to the atmospheric temperatures of the regions in Uranus probed by the same wavelengths, 90-120 K (cf. Buriez and de Bergh 1981). In addition, here the use of

a spectrum of Saturn as an intermediary is made possible by the fact that the effects of scattering on lines of CH_4 in the Saturn atmosphere have been studied by Buriez and de Bergh (1981) in a nearby spectral range ($1.1 \mu\text{m}$) where the CH_4 lines have been spectroscopically assigned (Pierre et al. 1980).

IV. ANALYSIS OF THE SPECTRUM OF URANUS

We have determined the abundance of CH_3D in the atmosphere of Uranus by fitting a synthetic spectrum to the 1982 observations described in section II. This approach requires the development of a model atmosphere that adequately accounts for the CH_4 absorptions in the $1.6 \mu\text{m}$ region as well as for the contribution of CH_3D . Since the low-temperature behavior of the weak methane lines has not been studied in the laboratory, the model further requires an empirical determination of the "effective" rotational quantum numbers for each of the contributing methane lines.

In this section we first outline this empirical determination of the J-assignments for the CH_4 lines observed at room temperature using our Saturn spectrum in place of the low-temperature laboratory spectrum. Secondly, we describe an atmospheric model for Uranus that adequately accounts for the CH_4 absorption in this region of the spectrum. Finally, we discuss our determination of the $\text{CH}_3\text{D}/\text{CH}_4$ mixing ratio.

a) "Rotational Assignments" for the CH₄ Lines Present in the Spectral

Range: 6413-6484 cm⁻¹

Using our room-temperature intensity measurements for the CH₄ lines and the nominal scattering model of Buriez and de Bergh (1981, shown in their Figure 7), we computed a synthetic spectrum for Saturn. The CH₄-H₂ line-broadening Lorentz width γ_0 at 295 K was assumed to be 0.075 cm⁻¹/atm for all lines (Varanasi 1971). We normalized the continuum level of this synthetic spectrum to the local continuum of Saturn in spectral ranges where planetary absorption appeared negligible, and the absorption by solar and telluric lines was estimated from the lunar spectrum recorded during the Saturn observing run.

Contributions to the spectrum by lines of the 3v₂ band of CH₃D are very weak. They were included in the model by adjusting the CH₃D abundance to provide a best overall fit to those lines that appear relatively free of CH₄ blends in our room-temperature CH₄ laboratory spectrum. Consistency with blended lines was also checked since these provide upper limits to the total CH₃D abundance. This procedure led to our adopted value of CH₃D/CH₄ $\sim 7 \times 10^{-5}$ for Saturn, in excellent agreement with the results derived by the analysis of the Voyager observations of the v₆ band at 8.6 μ m: $8.7^{+7.2}_{-6.7} \times 10^{-5}$ (Courtin et al. 1984). The details of the analysis are the topic of a separate paper (de Bergh et al. 1985).

After correction for any CH_3D contribution, the remaining differences between absorption strengths of the methane lines in this synthetic spectrum (dashed line) and in the observed Saturn spectrum (solid line), shown in Figure 3a, are due primarily to the low temperatures in Saturn's atmosphere. These differences were used to assign effective J-values to each of the CH_4 lines by determining the rotational population distribution required to match the two spectra while retaining Buriez and de Bergh's model parameters. In particular their total CH_4/H_2 mixing ratio and temperature profile. In these calculations we assumed a $1/T$ temperature dependence for the Lorentz width. Figure 3b compares the temperature-scaled synthetic spectrum (dashed line) and the observed one (solid line) of Figure 3a.

The accuracy of these "rotational assignments" relies strongly on the validity of the Buriez and de Bergh scattering model. Indeed, in the spectral range analyzed here, many of the CH_4 lines present are weaker than the lines from which the model was derived, increasing the uncertainty of the assignments. We searched for evidence of a manifold structure based on these J-values in hopes of confirming them, but unfortunately no recognizable patterns could be found. However, an attempt we have made to analyze the few strongest lines that are measurable in a 150 K, 48-meter, 250 torr spectrum of CH_4 recorded with the FTS at Meudon by Cuisenier and de Bergh (private communication) yields results quite consistent with the assignments we

have made for these lines based on the Saturn spectrum.

Blending of the CH_4 lines in the Saturn spectrum also affects our accuracy in assigning these rotational quantum numbers and increases the difficulty of the analysis in regions where it is particularly strong. One such region lies between 6433 and 6450 cm^{-1} , where we are unable to obtain very good agreement between the observed and synthetic spectra. In addition, we have detected a few very weak residual absorptions in the spectrum of Saturn for which our model cannot account. These unidentified absorptions do not correspond to any CH_4 features in our room-temperature laboratory spectrum or to any known CH_3D features, and they could not be assigned to any likely molecule such as NH_3 or C_2H_2 . Our calculations show that isolated CH_4 lines which are at or below the detection limit in our room-temperature spectrum could be enhanced sufficiently at low temperatures to explain the observed absorptions if their rotational quantum numbers are less than 3; but with the laboratory data in hand, it is not yet possible to model them satisfactorily. The existence of these features is a limitation to further refinements of our atmospheric model and adds an overall uncertainty to our analyses. Similarly weak features, undetected in our room-temperature laboratory spectrum, also could be blended with the observed CH_3D absorptions adding another source of uncertainty to our estimate of the CH_3D abundance in the outer planet atmospheres. This additional uncertainty

is particularly critical to our determination of a lower limit to the $\text{CH}_3\text{D}/\text{CH}_4$ ratio in the atmosphere of Saturn (de Bergh et al. 1985).

b) An Atmospheric Model for Uranus

Synthetic spectra of Uranus were computed for different atmospheric models, using as a line list the 610 lines of CH_4 detected in the range $6413\text{--}6484\text{ cm}^{-1}$ on the laboratory spectra, with J-values assigned on the basis of our Saturn-room temperature comparison described above. We determined the best model for Uranus by comparison with the Uranus spectrum that had been divided by the corresponding solar spectrum to eliminate solar and telluric contamination.

No spectral region in the Uranus spectrum is entirely devoid of absorptions. The continuum level in each model of the Uranus/Sun spectrum was defined as the minimum level above the region of least absorption (near 6345 cm^{-1}) that provided a satisfactory fit to the observations. This level ranged from 5 to 50 percent higher than the local maxima of the spectrum.

Our approach was to adopt the simplest atmospheric model that would account for the CH_4 absorptions in the regions of the observed spectrum free of possible CH_3D contributions. We considered three classes of models: reflecting-layer models (RLM), homogeneous scattering models (HSM), and two-cloud models (TCM). Although RLMS gave generally much better agreement with the observations than did

HSMs, the regions of the strongest absorptions, near 6425, 6430, and 6480 cm^{-1} , were consistently too deep in the synthetic spectrum. The addition of a tenuous haze with an optical thickness for isotropic scattering of $\tau \sim 0.05$ above the reflecting layer with a purely absorbing layer between, improved the agreement in these regions. In the best case there is no CH_4 above the haze. The continuum albedo of the haze in this TCM was assumed to be 0.7 (Fink and Larson 1979) while the lower cloud was treated as a Lambert surface.

At this spectral resolution, the synthetic spectra are not very sensitive to the effective pressure level of the absorbing layer, but there are a number of regions in the spectrum that constrain the range of model temperatures. In Figures 4a and 4b, we compare two of our models with different values of temperature to illustrate the effect. In each model the CH_4 abundance was adjusted to give the best agreement with the Uranus spectrum, and a comparison of the agreements acts as an effective temperature discriminator. Assuming an average atmospheric pressure of 1.5 atm, our best fit to the methane absorptions by this TCM was obtained for an average temperature of 110 K and a column density for CH_4 of 1.8 km-am between the two clouds. These parameters were adopted for our nominal model.

Although we selected the model that gave the best agreement with the observed methane absorptions considered free of possible CH_4 contamination, it lacked sufficient absorption in several other

spectral regions (cf. Figures 4a and 4b). The most obvious of these occur near 6427 and 6451 cm^{-1} , which corresponds precisely to the spectral ranges where the condensed Q-branch and the R(2) manifold of the $3\nu_2$ overtone of CH_3D absorb. These coincidences, which could not be explained by temperature effects, as demonstrated by the two models illustrated in Figures 4a and 4b, form the basis for its identification and analysis.

Using the CH_3D line intensities measured by Lutz (1985) and the spectroscopic assignments from Paper I, we included the effects of CH_3D in our nominal model. In addition to accounting for the additional absorption observed needed near 6427 and 6451 cm^{-1} , the inclusion of CH_3D in our model improved the agreement with observations of Uranus in other spectral ranges--the regions of the R(3), R(4), and R(5) manifolds. The best agreement, illustrated in this Figure 5b, was obtained with a $\text{CH}_3\text{D}/\text{CH}_4$ ratio of 3.6×10^{-4} .^a Figure 5a shows the synthetic spectrum obtained with no CH_3D for comparison.

The uncertainties in this ratio are difficult to assess quantitatively. However, consideration of the uncertainties in the

^aIn their paper discussing the possible identification of CH_3D in the atmospheres of Titan and Uranus, Lutz et al. (1981) investigated the effects of CH_3D on the spectrum of Uranus. Because of an error in the partition function, the value of the $\text{CH}_3\text{D}/\text{CH}_4$ ratio used in their models (cf. their Figure 3b) was actually a factor of three larger than quoted.

intensities of lines of both CH_4 and CH_3D ; uncertainties in the rotational assignments of the CH_4 features; uncertainties introduced by the use of an average pressure-broadening coefficient; uncertainties in the placement of the continuum level for the Uranus/Sun spectrum; and uncertainties in the selection of an atmospheric model for Uranus suggest that the accuracy of our $\text{CH}_3\text{D}/\text{CH}_4$ ratio in the atmosphere of Uranus is better than a factor of two.

V. DISCUSSION

In Table 1 we have summarized the recent measurements of the $\text{CH}_3\text{D}/\text{CH}_4$ ratio in the atmospheres of the outer planets, including our own for Uranus and de Bergh *et al.*'s for Saturn. For both Jupiter and Saturn the most recent estimates show excellent self-consistency in spite of the varied techniques and the different spectral regions in which they were employed. In addition, a comparison of Jupiter and Saturn suggests a systematic difference between them by perhaps a factor of two, although the large uncertainties associated with each measurement make a definitive claim somewhat tenuous.

An enhancement of the $\text{CH}_3\text{D}/\text{CH}_4$ ratio in the atmosphere of Uranus relative to Saturn and possibly Jupiter, however, seems more certain. Substantial enrichments of D/H ratios in the present-day atmospheres of Uranus and Neptune compared to Jupiter and Saturn are expected if

low-temperature, equilibrium partitioning of deuterium occurred among the various volatiles that condensed out of the cold protosolar nebula to form the icy component of their cores, and if the subsequently accreted hydrogen-helium outer envelopes of the planets are mixed with the deeper layers where the deuterium-enriched volatiles reside (Hubbard and MacFarlane 1980). Since the maximum masses of these ices in the cores of Jupiter and Saturn are small compared to the masses of their respective deep hydrogen and helium envelopes, mixing with the deuterium-enriched volatiles has little effect on the D/H ratio in the hydrogen component of their atmospheres. In contrast, Uranus and Neptune have thin outer envelopes with masses on the order of only 10% of that of the ices, and mixing can substantially alter their atmospheric compositions.

Whether this proposed primordial deuterium fractionation is responsible for the apparent differences in the planetary $\text{CH}_3\text{D}/\text{CH}_4$ ratios is unclear, especially since optical studies of HD and H_2 absorptions yield D/H ratios which are essentially identical for each atmosphere (Trafton and Ramsay 1980; Macy and Smith 1978; McKellar, Goetz, and Ramsay 1976). This latter anomaly could be explained if the deuterium in methane has not yet reached a new fractionation equilibrium with that in hydrogen in the present-day atmospheres of one or more of the planets, but in view of the warm temperatures in the atmospheres, disequilibrium is not expected.

In Table 2 we compare the range of D/H ratios consistent with all the published HD/H₂ measurements with similar ranges for D/H in methane derived from the CH₃D/CH₄ observations in Table 1. The stoichiometric relationships used,

$$[D/H]_{H_2} = (1/2)HD/H_2$$

$$[D/H]_{CH_4} = (1/4)CH_3D/CH_4,$$

assume that higher order deuterium substitutions are insignificant. Based on improved molecular parameters for H₂ (Bragg, Brault, and Smith 1982), Cochran and Smith (1983) have proposed an increase in the D/H ratios for the three planets listed in Table 2 by nearly a factor of two, and Trauger's (1935) preliminary D/H ratio of $(7.1 \pm 1.0) \times 10^{-5}$ for Jupiter is in agreement with this proposal. However, Trauger's (1985) estimate for Uranus suggests a value closer to the lower limit given in Table 2.

Under equilibrium conditions, these two measures of the atmospheric D/H ratios are related by

$$[D/H]_{H_2} = (1/f)[D/H]_{CH_4},$$

where f is the "fractionation factor" which describes the enhancement of deuterium in methane over that in molecular hydrogen. The range in values of f has a lower bound of 1 (corresponding to the high temperature asymptote) simply because the equilibrium kinetics always favor deuterium in the methane phase. In the catalysis-free gas phase, it has an upper bound of 1.8 that corresponds to a temperature below

which the exchange reactions are too slow for equilibrium to have been achieved in the age of the Solar System (Beer and Taylor 1973, 1978).

The comparison of $[D/H]_{CH_4}$ to $[D/H]_{H_2}$ suggests that such equilibrium may not be established in the atmospheres of Jupiter and Saturn, although the observed differences between their $[D/H]_{CH_4}$ ratios could be due to the exchange reactions slowly proceeding further towards partial completion on Jupiter. Interior differences between these two highly similar planets has already been proposed to explain the apparent depletion of helium in the atmosphere of Saturn compared to Jupiter (Stevenson and Salpeter 1977a,b). If the higher $[D/H]_{H_2}$ values suggested by Cochran and Smith (1983) and by Trauger (1985) prove to be true, then this evidence for a decoupling of the H_2 - CH_4 deuterium-exchange reactions in these atmospheres seems even more certain. Since there is too much hydrogen in the deep outer envelopes of Jupiter and Saturn to be significantly perturbed by the volatiles that outgas from the cores of these planets, substantial depletions (enhancements) of H_2 (HD) relative to HD (H_2) must have occurred in the atmosphere over the lifetime of the planets or the disequilibrium must have been established in the protosolar nebula.

Super-solar C/H ratios are observed in the atmospheres of Jupiter and Saturn. These apparent enhancements are sometimes ascribed to outgassing by the methane-rich planetary cores or to possible accretions of methane-rich planetesimals (Gautier and Owen 1983b).

However, for any such methane enrichment process to also effect a factor of two reduction of the D/H ratio in the atmospheric methane, the methane in the planetary cores or planetesimals would have to be nearly deuterium free, in contradiction to our study of Uranus, from which we expect the methane in the cores to be enriched in deuterium. A depletion of H_2 relative to HD in the atmosphere or in the protosolar nebula can account for the discrepancy, but it is hard to see how this would come about. Furthermore, a hydrogen depletion would lead to He/H ratios in the atmospheres which are greater than solar, again contrary to observation.

Our observations of Uranus form a different case. The D/H ratio in its atmospheric methane is substantially larger than found for the Jovian planets, and within the uncertainties, the ratio of the $[D/H]_{CH_4}$ to $[D/H]_{H_2}$ values is consistent with the fractionation equilibrium constraints discussed above, $1.0 < f < 1.8$. However, the precision of the measurements does not rule out a simple CH_3D enhancement decoupled from any deuterium-exchange with HD.

The Uranian atmosphere appears to be strongly enriched in methane compared to the Jovian planets, as would be expected if outgassed volatiles trapped in the core ices of Uranus contributed significantly to the composition of its outer, thinner hydrogen envelope. The co-enrichment of CH_3D appears to support this interpretation as well as the Hubbard-MacFarlane postulate of deuterium enhancement in the

methane ices of the core, independent of whether subsequent fractionation equilibrium of deuterium in the atmosphere has been attained.

Uranus, with its lack of interior heat sources to drive convection, is less likely to establish fractionation equilibrium than Jupiter and Saturn. Since the observations of Jupiter and Saturn appear to contradict such equilibration or support only partial completion of deuterium exchange, our measurement for Uranus may represent the $\text{CH}_3\text{D}/\text{CH}_4$ ratio in the primordial ices, with little or no change since the planet formed.

However, if the deuterium exchange reactions have proceeded to completion and fractionation equilibrium has been established in the Uranian atmosphere, the interpretation is less clear. Indeed, even the direction of equilibration would then be uncertain, and we could place only an upper limit on the $[\text{D}/\text{H}]_{\text{CH}_4}$ ratio in the ices of Uranus.

For example, if we assume that the atmospheric methane on Uranus is dominated by the contribution from the core ices, and if we adopt a CH_4/H_2 mixing ratio of about 0.015, (0.03) and a $\text{CH}_3\text{D}/\text{CH}_4$ mixing ratio in the ices of 3.7×10^{-3} , (2×10^{-3}), deuterium exchange would have yielded a deuterium enrichment of the molecular hydrogen component of the atmosphere of a factor of two over the accreted value. The close similarities of the $[\text{D}/\text{H}]_{\text{H}_2}$ ratios observed for Jupiter, Saturn, and Uranus suggest that an enrichment of this order of magnitude has not

occurred for Uranus.

V. SUMMARY

In this paper we have presented new observations of the spectrum of Uranus at 1.6 μm and have identified CH_3D as a contributor to the absorption in that region. Our analysis of this spectrum, along with new laboratory data on both CH_4 and on CH_3D , yielded a $\text{CH}_4/\text{CH}_3\text{D}$ mixing ratio of $(3.6^{+3.6}_{-1.8}) \times 10^{-4}$, corresponding to a D/H ratio of $(9^{+9}_{-4.5}) \times 10^{-5}$ in atmospheric methane.

A comparison of these results with published determinations of the $\text{CH}_3\text{D}/\text{CH}_4$ ratio in the atmospheres of Jupiter and Saturn along with similar values for HD/H_2 led to a number of conclusions and speculations about the effectiveness of gas-phase exchange reactions in establishing deuterium fractionation equilibrium, and the relationship between present-day and protosolar abundance ratios:

1. The $\text{CH}_3\text{D}/\text{CH}_4$ mixing ratio in the atmosphere of Uranus is substantially larger than that observed for Jupiter and Saturn, consistent with the view that volatiles trapped in the core ices of Uranus have contributed significantly to its present-day atmosphere and with the postulate that these volatiles are enhanced in deuterium.

2. The D/H ratios in methane and molecular hydrogen are consistent with fractionation equilibrium of deuterium in the

atmosphere of Uranus, but circumstantial evidence suggests that this agreement may be coincidental and the $\text{CH}_3\text{D}/\text{CH}_4$ mixing ratio may be a direct measurement of the composition of the core ices.

3. The D/H ratios in methane and in molecular hydrogen in the atmospheres of Jupiter and Saturn may not be consistent with deuterium fractionation equilibrium, and the $\text{CH}_3\text{D}/\text{CH}_4$ mixing ratios may represent the composition of the nebular gases out of which the planetary atmospheres accreted.

4. The depleted $\text{CH}_3\text{D}/\text{CH}_4$ ratios in the atmospheres of Jupiter and Saturn cannot be plausibly explained by the methane enrichment processes usually invoked to account for the observed enhancement of atmospheric C/H ratios, but a depletion of H_2 relative to HD could account for both super-solar C/H ratios and sub-equilibrium $\text{CH}_3\text{D}/\text{CH}_4$ ratios.

These four conclusions are by their nature speculative, but they do outline some fundamental problems in the study of the formation and evolution of our Solar System. They also indicate the depth to which these problems can be probed if the accuracy of these measurements can be improved sufficiently to discriminate between the various pathways by which the interpretive logic can proceed.

The lack of low-temperature, high-resolution, high signal-to-noise laboratory measurements of the weak methane lines in the $1.6 \mu\text{m}$ region is an important source of uncertainty in the current

analyses of the CH_4/CH_3 ratios in outer planet atmospheres and is a major limitation in future analyses. Improvements in model atmospheres and in the treatment of the radiative transfer are also necessary, but the implementation of such improvements may require planetary spectra of both higher resolution and signal-to-noise ratios.

Estimates of the HD/H_2 ratio are also highly imprecise and limit the interpretation of the observations. Improvements here depend strongly on advances in our knowledge of radiative transfer processes in the atmosphere, as well as in defining the atmospheric structures accurately.

With progress in these areas, more stringent tests of models of planetary formation and evolution will be possible, and perhaps we can begin to understand the processes that have led to the Solar System as we know it today.

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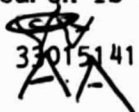


TABLE 1

OBSERVED CH₃D/CH₄ RATIOS IN OUTER PLANET ATMOSPHERES

Object	10 μ m region	5 μ m region	1.6 μ m region
Jupiter	$1.7 \pm 0.3 \times 10^{-4}$ ^a	$1.2 \pm 0.7 \times 10^{-4}$ ^b
Saturn	$8.7^{+7.2}_{-6.7} \times 10^{-5}$ ^c	1.5×10^{-5} ^d	$-7^{+7.0}_{-4.5} \times 10^{-5}$ ^e
Uranus	$3.6^{+3.6}_{-1.8} \times 10^{-4}$ ^f

^aKnacke et al. (1982), adopting CH₄/H₂ = 2.2×10^{-3} (Gautier and Owen 1983).

^bKunde et al. (1982); Drossart et al. (1982); Beer and Taylor (1973, 1978), adopting CH₄/H₂ = 2.2×10^{-3} , (Gautier and Owen 1983).

^cCourtin et al. (1984).

^dFink and Larson (1978), revised for CH₄/H₂ = 4.5×10^{-3} (Courtin et al. 1984), uncertainty estimate not given.

^ede Bergh et al. (1985).

^fThis work.

TABLE 2
OBSERVED D/H RATIOS IN OUTER PLANET ATMOSPHERES

	Jupiter	Saturn	Uranus
$[D/H]_{H_2}$	$4.2-7.0 \times 10^{-5}{}^a$	$2.6-8.4 \times 10^{-5}{}^b$	$3.3-5.3 \times 10^{-5}{}^c$
$[D/H]_{CH_4}$	$3.6-4.8 \times 10^{-5}{}^d$	$0.6-3.5 \times 10^{-5}{}^d$	$4.5-18. \times 10^{-5}{}^d$

^aMcKella, Goetz, and Ramsay (1976).

^bMacy and Smith (1978).

^cMacy and Smith (1978); Trafton and Ramsay (1980).

^dSee Table 1.

REFERENCES

- Beer, R., and Taylor, F. W. 1973, Ap. J., 179, 309.
- _____. 1978, Ap. J., 219, 763.
- Bragg, S. L., Brault, J. W., and Smith, W. H. 1982, Ap. J., 263, 994.
- Buriez, J. C., and de Bergh, C. 1981, Astro. Ap., 94, 382.
- Cochran, W. D., and Smith, W. H. 1983, Ap. J., 271, 859.
- Courtin, R., Gautier, D., Marten, A., and Bezard, B. 1984, Ap. J., 287, 899.
- de Bergh, C., et al. 1985 (to be published).
- Drossart, P., Encrenaz, T., Kunde, V., Hanel, R., and Combes, M. 1982, Icarus, 49, 416.
- Fink, U., and Larson, H. P. 1978, Science, 201, 343
- _____. 1979, Ap. J., 233, 1021.
- Gautier, D., and Owen, T. 1983, Nature, 304, 691.
- Hubbard, W. B., and MacFarlane, J. J. 1980, Icarus, 44, 676.
- Knacke, R. F., Kim, S. J., Ridgway, S. T., and Tokunaga, A. T. 1982, Ap. J., 262, 388.
- Kunde, V. G., Hanel, R., Maguire, W., Gautier, D., Baluteau, J. P., Marten, A., Chedin, A., Husson, N., and Scott, N. 1982 Ap. J., 263, 443.
- Lutz, B. L. 1985 (to be published).
- Lutz, B. L., de Bergh, C., and Maillard, J. P. 1983, Ap. J., 273, 397.
- Lutz, B. L., de Bergh, C., Maillard, J. P., Owen, T., and Brault, J.

1981, Ap. J. (Letters), 248, L141.

Macy, Jr., W., and Smith, W. H. 1978, Ap. J. (Letters), 222, L73.

McKellar, A. R. W., Goetz, W., and Ramsay, D. A. 1976, Ap. J., 207,
663.

Pierre, G., Hilico, J. C., de Bergh, C., and Maillard, J. P. 1980, J.
Mol. Spec., 82, 379.

Stevenson, D., and Salpeter, E. 1977a, Ap. J. Suppl., 35, 221.

_____. 1977b, Ap. J. Suppl., 35, 239.

Trafton, L., and Ramsay, D. A. 1980, Icarus, 41, 423.

Trauger, J. 1985 (private communication).

Varanasi, P. 1971, J.Q.S.R.T., 11, 1711.

FIGURE CAPTIONS

Figure 1. Comparison between a laboratory spectrum of CH_4 , recorded with the FTS at the National Solar Observatory ($P = 200$ torr, pathlength: 434 m, $T = 294$ K) and a synthetic spectrum based on our line-intensity measurements and a unique pressure-broadening coefficient assumed equal to $0.085 \text{ cm}^{-1}/\text{atm}$.

Figure 2. Contribution of CH_3D to the absorption in the same laboratory spectrum of CH_4 , as in Figure 1. The spectral range shown here is the region of the Q-branch of the $3\nu_2$ band of CH_3D .

Figure 3. Illustration of the method we used to rotationally assign the CH_4 lines.

(a) Full line: the observed Saturn spectrum recorded in 1981 at KPNO with the FTS at the 4-meter telescope, after division by a lunar spectrum. Dashed line: synthetic spectrum of Saturn corresponding to the nominal Buriez and de Bergh (1981) scattering model with $\text{CH}_4/\text{H}_2 = 3.5 \times 10^{-3}$ and using the room-temperature line intensities of CH_4 , determined as explained in section III of this paper.

(b) Full line: same as in (a). Dashed line: synthetic spectrum of Saturn corresponding to the same scattering model; the

variation with temperature of the line intensities is taken into account and, for each line, the assigned J-value is the one that gives the best agreement between synthetic and observed absorption lines. The lines of CH_3D have been included in both synthetic spectra; with intensities and rotational assignments as explained in the text, they correspond to a $\text{CH}_3\text{D}/\text{CH}_4$ ratio of 6.8×10^{-5} . The hatched areas in Figure 3(b) show the contributions of CH_3D to the total absorptions.

Figure 4. (a) and (b) Full line: spectrum of Uranus recorded in 1982 June at KPNO with the FTS at the 4-meter telescope, divided by the spectrum of diffuse solar radiation recorded during the same run.

Dashed line: Synthetic spectra of Uranus computed for two different values of the the temperatures $T = 90 \text{ K}$ (a) and $T = 140 \text{ K}$ (b) and the two-cloud model described in section IV and including only CH_4 absorptions. In each case, the continuum level and the methane abundance selected are those that produce the best agreement between observed and synthetic spectra of Uranus.

Figure 5. Comparison between observed and synthetic Uranus spectra.

(a) and (b) Full line: spectrum of Uranus recorded in

1982 June at KPNO with the FTS at the 4-meter telescope, divided by the spectrum of diffuse solar radiation recorded during the same run.

(a) Dashed line: synthetic spectrum of Uranus computed as explained in section IV for only CH_4 absorptions, based on our normal atmospheric model (a temperature of 110 K, and a total methane abundance of $1.8 \text{ km} \cdot \text{atm}$, at an average pressure of 1.5 atm).

(b) Dashed line: synthetic spectrum of Uranus as shown in (a) but with CH_3D absorptions included: $\text{CH}_3\text{D}/\text{CH}_4 = 3.6 \times 10^{-4}$. The regions of the main $\text{CH}_3\text{D}-3\nu_2$ absorptions are indicated at the top of the figure.

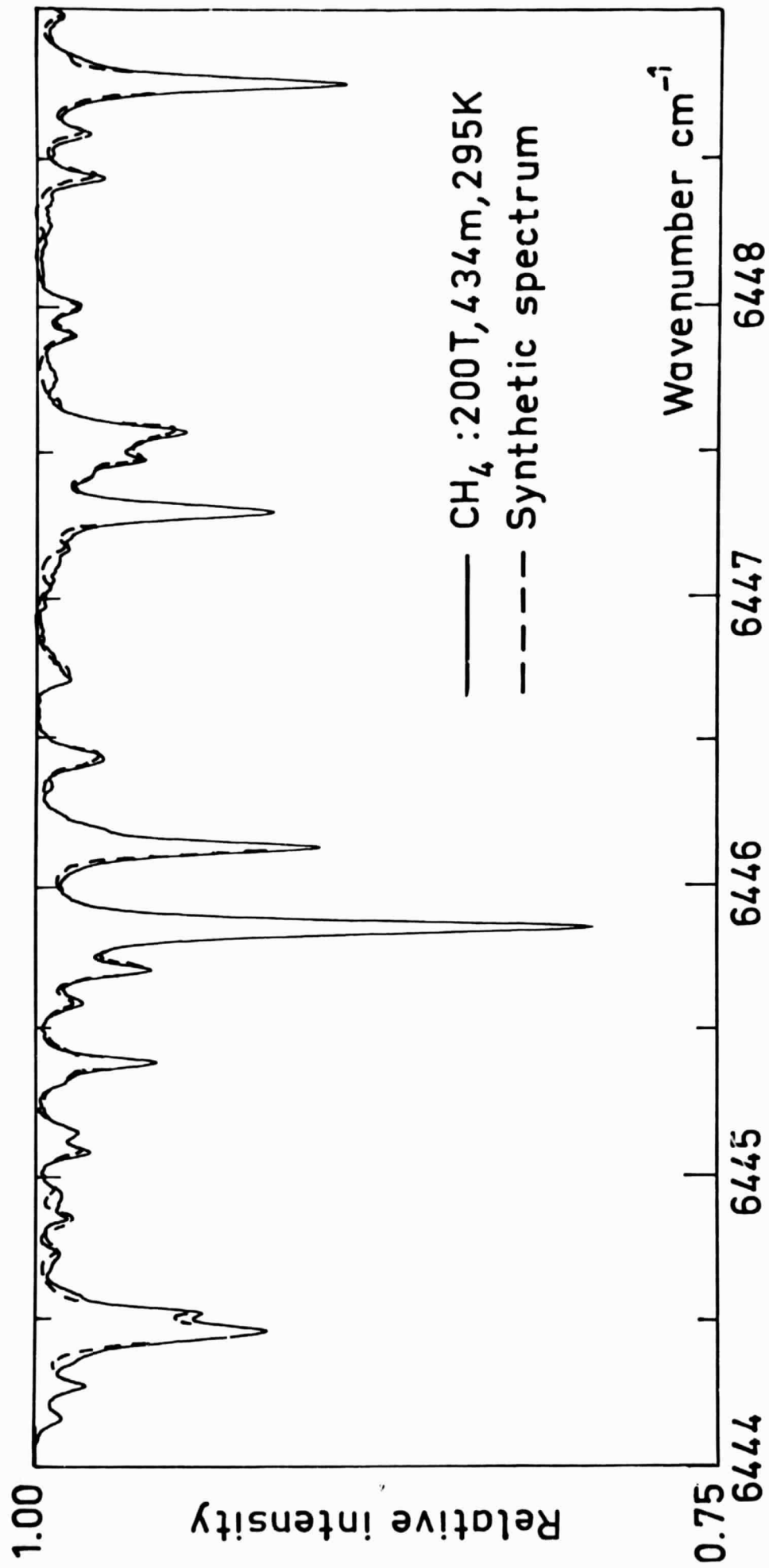


FIGURE 1.

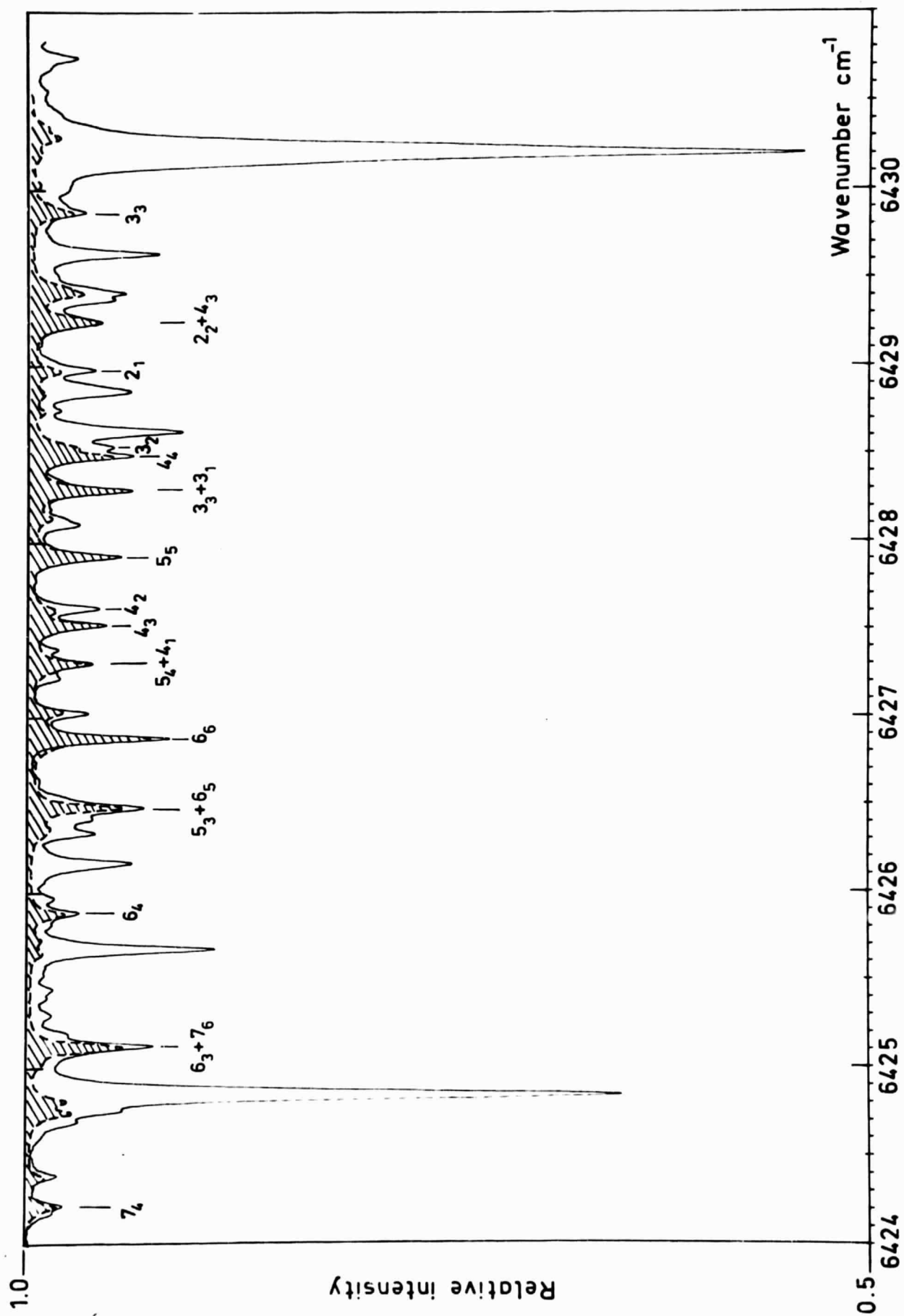


FIGURE 2.

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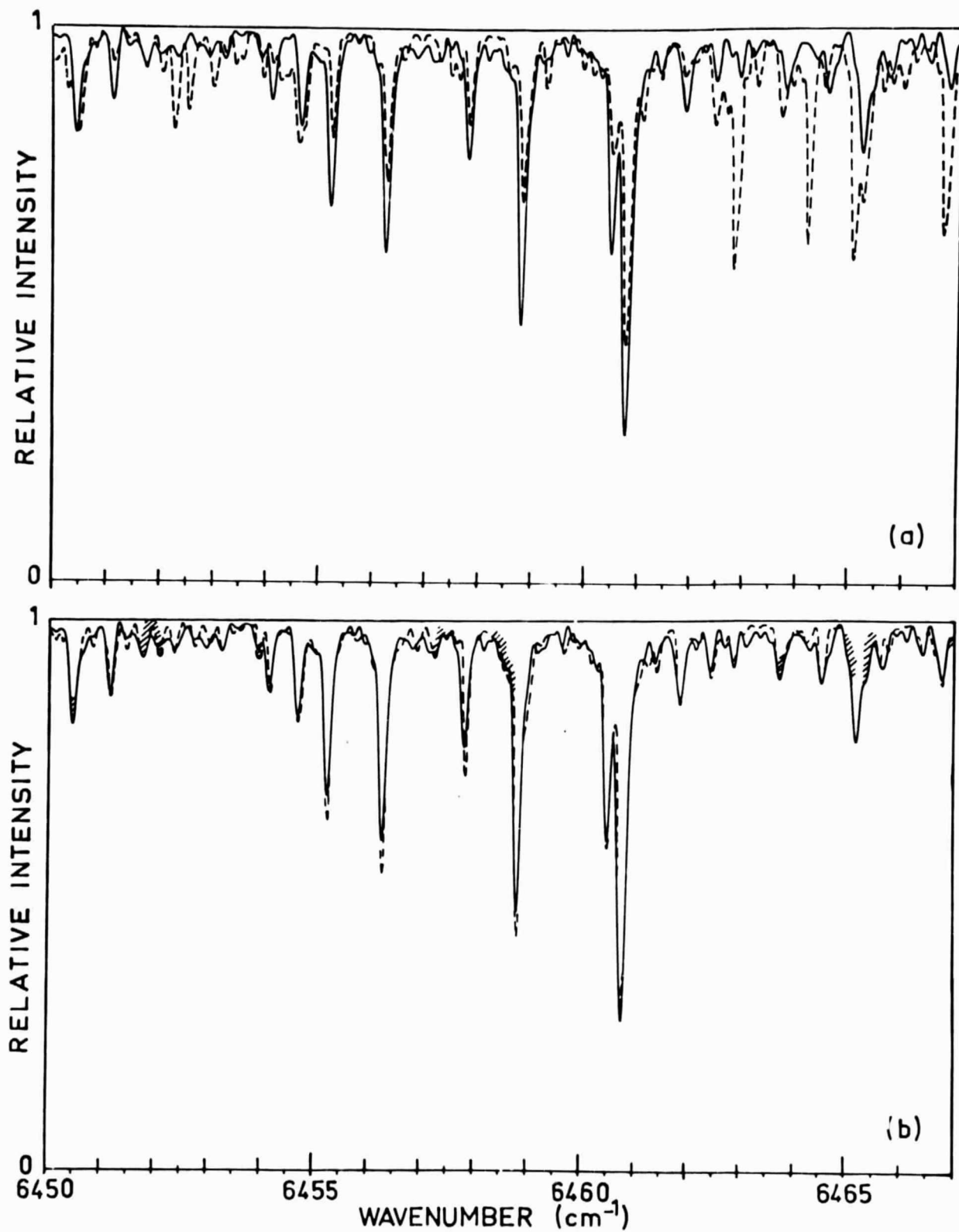


FIGURE 3.

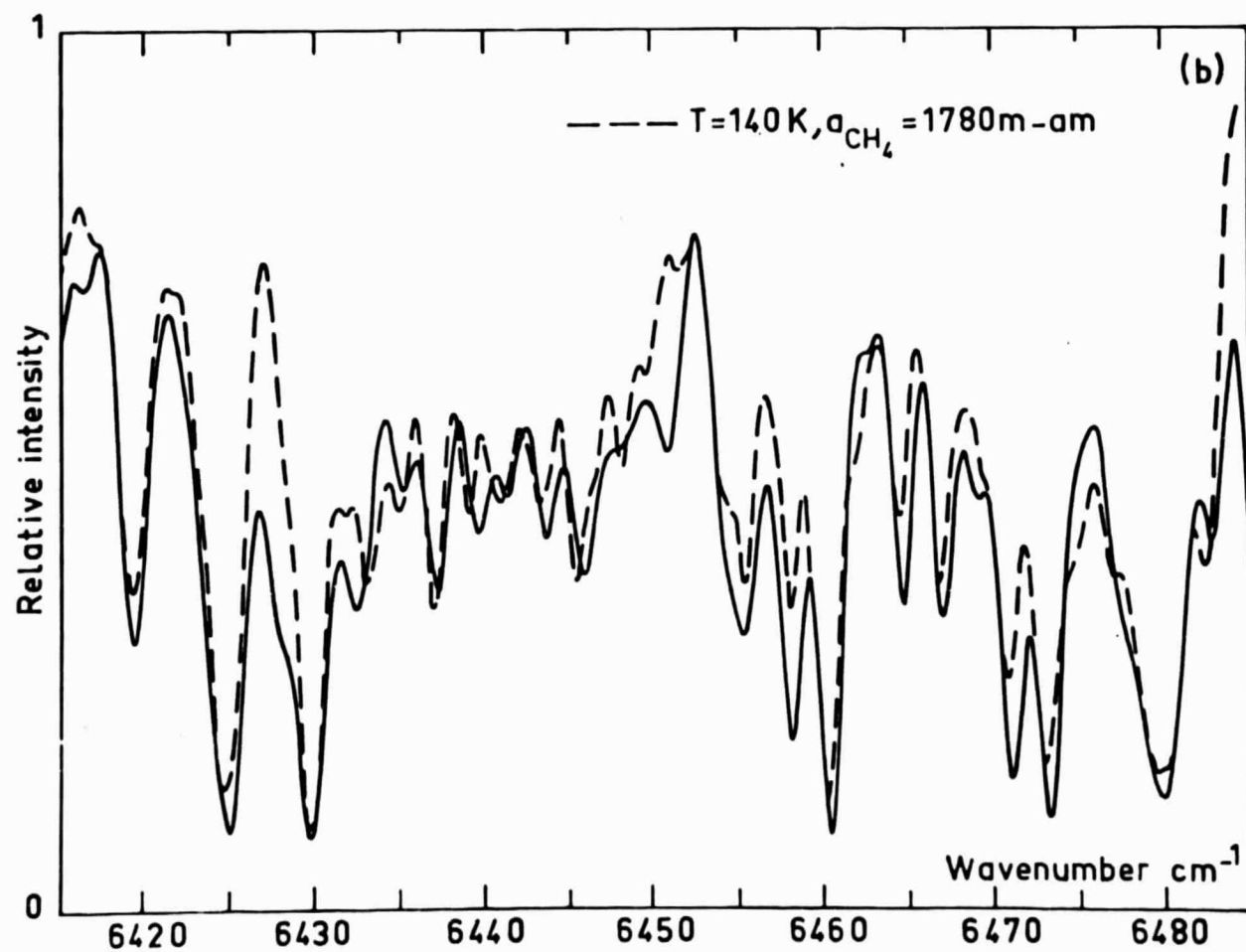
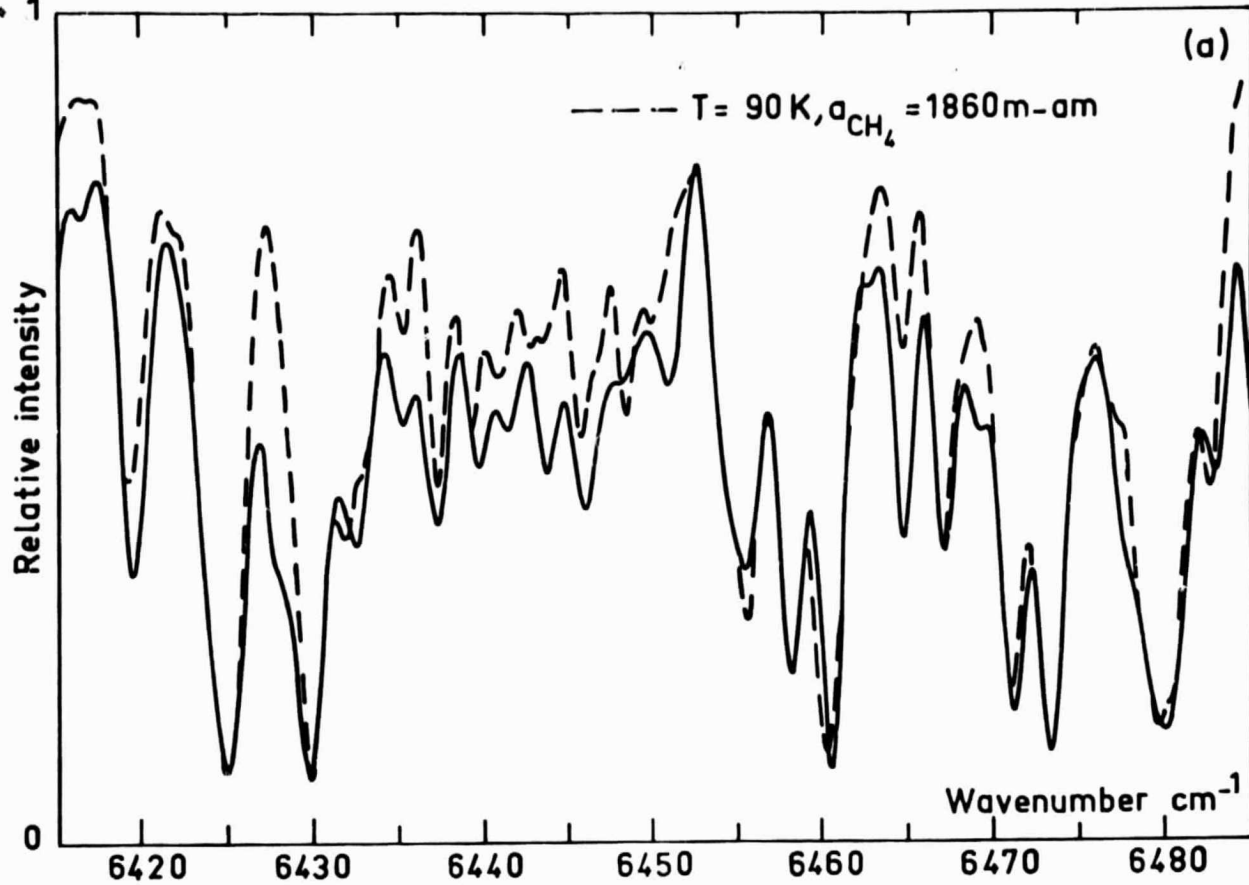


FIGURE 4.

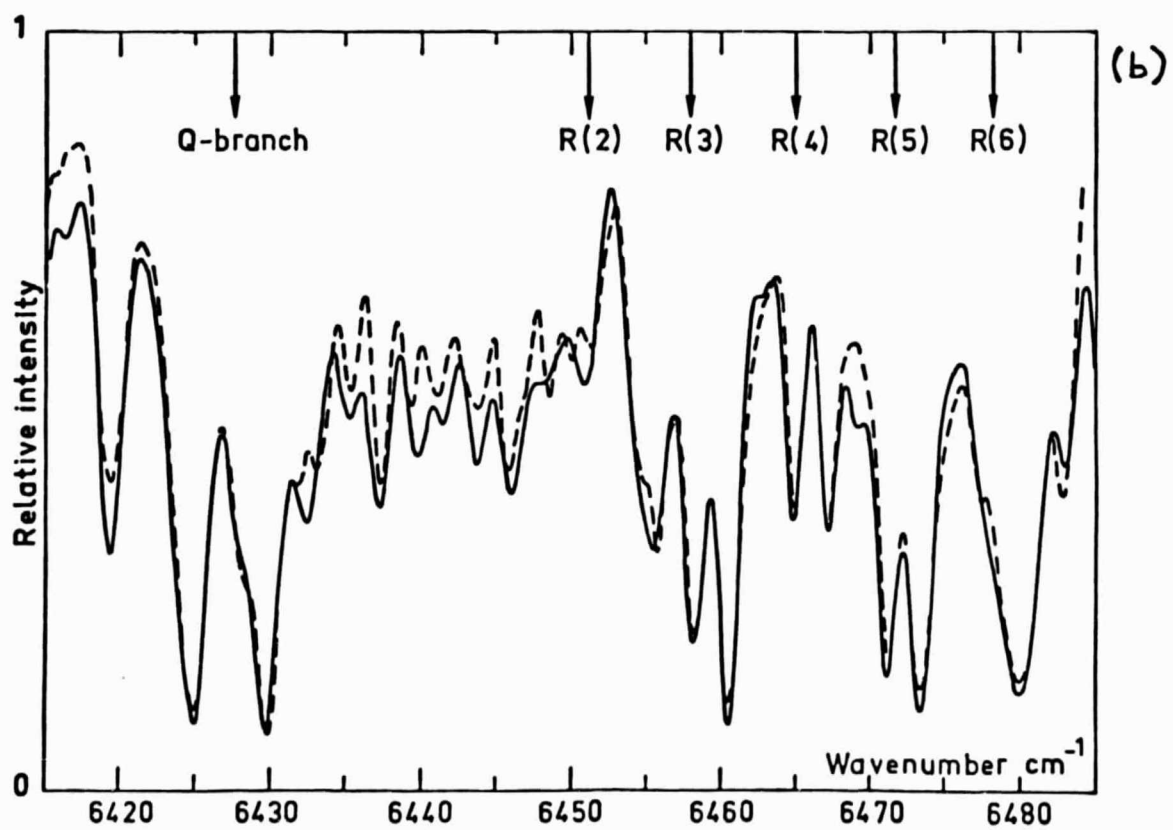
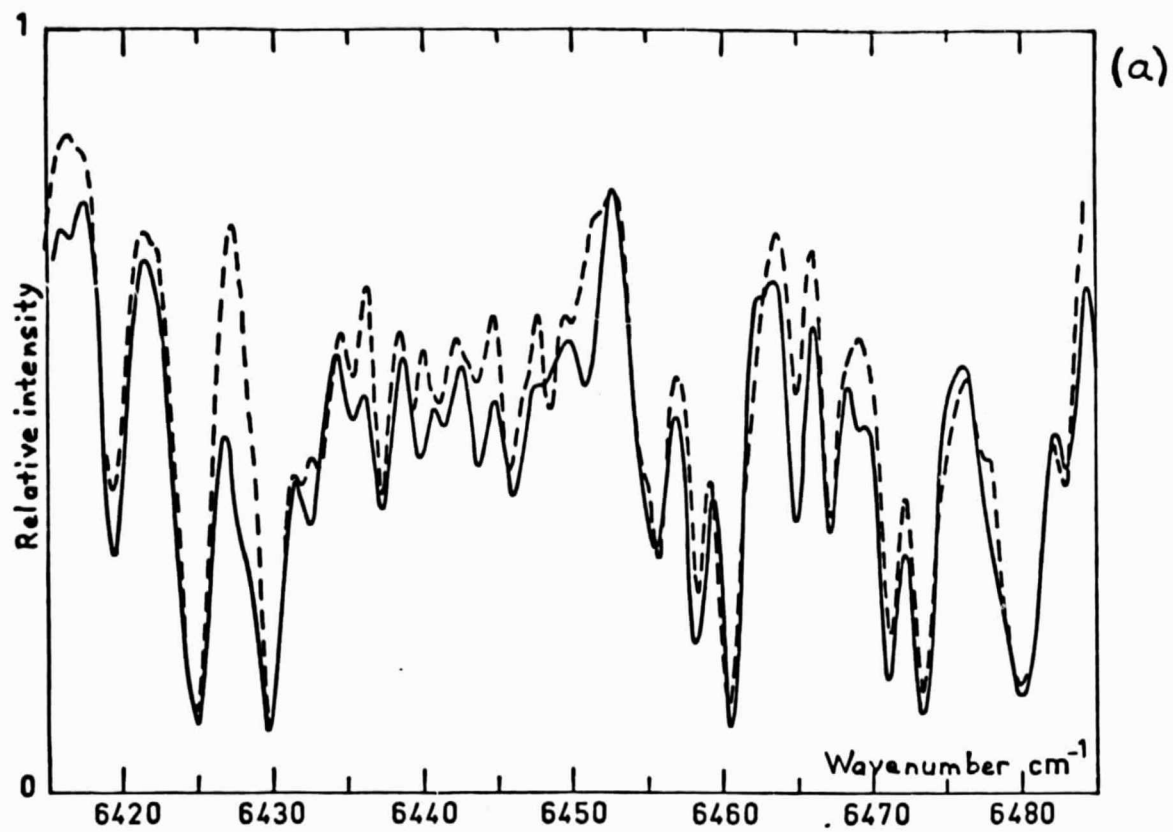


FIGURE 5.